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Self-Assembly of Individually Addressable Complexes of C_{60} and Phthalocyanines on a Metal Surface: Structural and Electronic Investigations

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The hosting properties of a close-packed layer of phenoxy-substituted phthalocyanine derivatives adsorbed on Ag(111) were investigated for the adsorption of C_{60} molecules. The C_{60} molecules bind to two clearly distinguishable sites, namely, to the underlying metal substrate in between two adjacent phthalocyanine derivatives, leading to structural and electronic properties analogous to those of C_{60} adsorbed on Ag(111), and to the core of the underlying phthalocyanine derivative, indicative of the formation of 1:1 donor−acceptor (D−A) dyads through a true host−guest interaction. The electronic properties have been determined by scanning tunneling spectroscopy measurements on individual D−A dyads.

The overwhelming interest in molecular organic materials in the recent past is mainly driven by the need to find novel materials with tunable attractive properties. The development of such materials contributes to the rapid progress in fields such as (opto)electronics, photonics, light harvesting, and so forth.[1−5] Molecules like C_{60}[6,7] and phthalocyanines,[8] which feature an aromatic π-system, are promising building blocks for the construction of molecular materials with unique electrochemical and photophysical properties. For instance, among the vast number of possible donor−acceptor (D−A) complexes, the combination of C_{60} and phthalocyanines[9,10] is of particular interest for potential applications in molecular electronics and light harvesting.[11,12] In fact, one of the most efficient organic photovoltaic devices reported to date was fabricated using a heterojunction based on copper phthalocyanine and C_{60}.[13,14]

Numerous studies have been performed to investigate D−A complexes either in solution or in their bulk form.[15,16] However, only scanning probe microscopy investigations offer the possibility to obtain information on both the structure and the electronic properties on the level of individual complexes formed at interfaces. In particular, the spectroscopic mode of the scanning tunneling microscope (STM) is useful for acquiring truly local information about the electronic properties.[17] This information in turn is crucial for a better comprehension of the interaction between C_{60} and phthalocyanines.

Up to now, most of the experiments investigating individually addressable D−A complexes on surfaces have been performed at the solid−liquid interface.[18−20] Yet, in this case, the assembly and the structure of the complex, as well as its electronic properties, is affected by the solvent and the solutes. On the other hand, a solvent-free environment is more suitable for both potential future applications and the direct comparison of experiments with numerical simulations. Only a handful of experiments were carried out in a solvent-free environment,[21−24] and none of them feature the electronic interaction of the π-conjugated segments of the constituents at room temperature.

Here, we present the hosting properties of an ordered layer of phthalocyanine (Pc) derivatives adsorbed on a Ag(111) surface for the adsorption of C_{60}. The C_{60} molecules adsorb at two clearly distinguishable positions on the predeposited Pc layer; they are in contact either with the metal substrate in between two adjacent Pc molecules or with the Pc core. The latter case is made possible through a unique modification of the phthalocyanine, which constrains the C_{60} to be located directly above the π-conjugated Pc core. Hence, the presented system combines the three following features: (i) the direct electronic interaction between donor and acceptor moieties, (ii) the formation by self-assembly, and (iii) thermal stability. The combination of these features is vital for the direct investigation of a single D−A complex. In addition, to our knowledge, this is the first case for C_{60} spontaneously binding to the core of an underlying macrocycle, that is, the Pc molecule adsorbed on a surface in a solvent-free environment.

The Pcs are symmetrically octasubstituted with di(tert-butyl)phenoxy (DTPO) groups (referred to as ZnPc-DTPOs in the following),[25] and their self-organization on both Ag(111) and Au(111) surfaces has been previously discussed in detail.[26] The experiments were carried out under ultrahigh vacuum (UHV) conditions with a low-temperature STM operated at 77 K. The samples were prepared at room temperature in situ by

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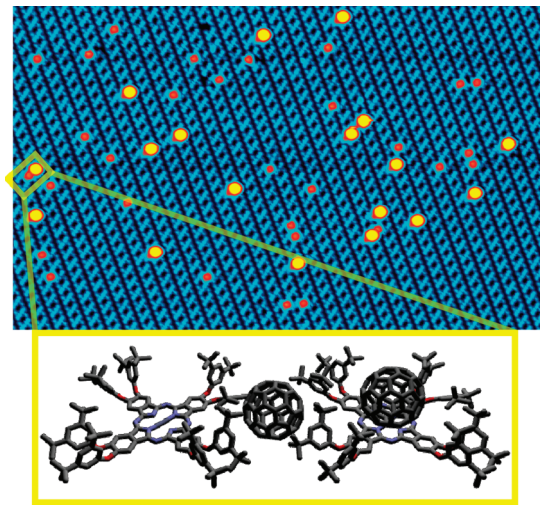

Figure 1. Top: STM image (80 × 50 nm^2, 20 pA, 1 V, 77 K) of C_{60} molecules (peripheral in red and central in yellow) adsorbed onto an ordered layer of ZnPc-DTPOs (in blue). Bottom: 3D model of the molecules marked by the yellow rectangle in the STM image with the peripheral C_{60} in the middle and the central C_{60} on the right.

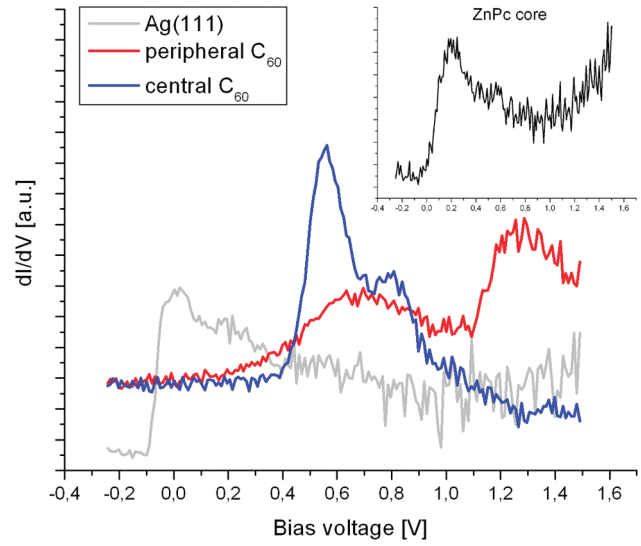

Figure 3. Scanning tunneling spectroscopy data: dI/dV spectra taken on the clean Ag(111) surface (gray), the peripheral C_{60} (red), and the central C_{60} (blue). Inset: dI/dV spectrum for ZnPc-DTPO taken above the central core of an individual molecule.

thermal evaporation of the molecules from a commercial Knudsen cell type evaporator. For all experiments, the densest phase of the ZnPc-DTPOs was prepared (labeled phase III in ref 26).

Figure 1(top) shows a representative STM image for C_{60} deposited onto an ordered unmodified layer of ZnPc-DTPOs. A tentative 3D model demonstrating the approximate relative positions of the molecules marked by the yellow rectangle in the STM image is shown in Figure 1(bottom). The C_{60} bound to the core of the ZnPc-DTPO (referred to as central C_{60} in the following) appears as a bright dot (yellow in Figure 1(top)) in the STM image, while the C_{60} bound to the substrate in between two ZnPc-DTPOs belonging to adjacent molecular rows (referred to as peripheral C_{60} in the following) appears less pronounced (smaller red dot in Figure 1(top)) in the STM image. The apparent height of the peripheral C_{60} is in agreement with earlier observations for C_{60} adsorbed on Ag(111),[27] whereas the central C_{60} appears about 3 Å higher.[28]

By performing controlled repositioning experiments, we demonstrate that the central and the peripheral C_{60} are adsorbed on an intact, defect-free ZnPc-DTPO layer. Molecular repositioning experiments for the ad-C_{60} molecules are carried out by switching off the STM feedback system and setting a negative tip-lift value of 0.2 nm for the central C_{60} and 0.5 nm for the peripheral C_{60}. This means that once the feedback is switched off, the tip is approached 0.2 nm (0.5 nm) toward the sample surface. Herein, this distance is measured relative to the initial z height, which is defined by the combination of the current setpoint and bias voltage, in our case, 10 pA and 0.5 V. Then, the tip is laterally moved in order to "push" the C_{60} in the desired direction in the so-called "constant height manipulation mode".[29] In Figure 2, a series of manipulation events is summarized. The first frame features a central C_{60} appearing as a bright lobe covering the underlying ZnPc-DTPO. The successive STM image in the second frame shows that the central C_{60} was moved to a peripheral position. Another molecular repositioning was performed, but this time, the C_{60} was pushed ~5 nm toward the top of the image (see arrow in Figure 2) to a position outside of the third imaged frame.

The central and the peripheral C_{60} exhibit significantly different electronic properties in our investigations by means of scanning tunneling spectroscopy (STS) (Figure 3). For these measurements, the bias voltage is modulated with an AC amplitude (typically around 10 mV rms) which is considerably

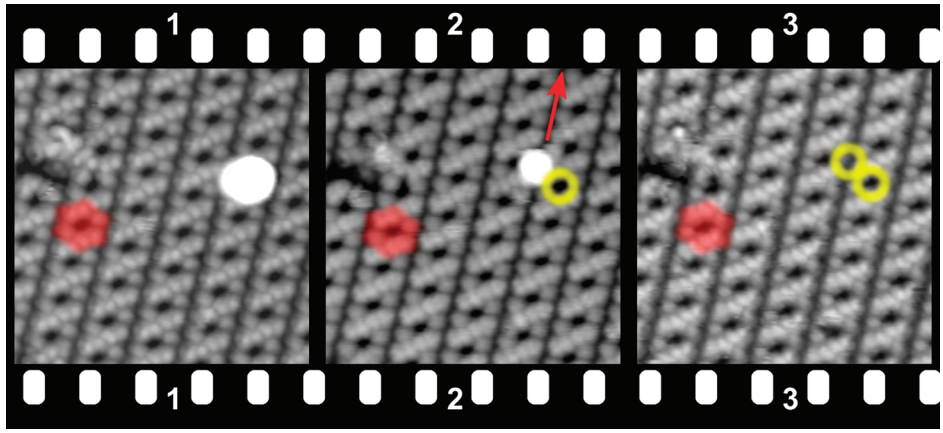

Figure 2. Sequence of three consecutive STM images (14 × 14 nm^2, 10 pA, 0.5 V, 77 K) displaying controlled manipulation of C_{60} adsorbed on the ZnPc-DTPO layer. The yellow circles mark the position of the C_{60} in the preceding images. One ZnPc-DTPO has been highlighted in red in each STM image to serve as a reference position.

smaller than the peak line width. With a lock-in amplifier, the differential conductivity (d*I*/d*V* signal) is obtained, which is proportional to the local density of states. The PtIr tip is cleaned by a field emission procedure, and its electronic structure is checked by recording the d*I*/d*V* spectrum for the clean Ag(111) surface. For our STS experiments, only tips clearly capable of resolving the well-known onset for the surface state (gray curve in Figure 3)[30] were chosen since this provides a good reference to ensure the cleanliness of the tip and the reproducibility of the experiments.

The d*I*/d*V* spectrum of the peripheral C_{60} (red curve in Figure 3) exhibits two clearly resolved peaks at ~0.7 and 1.3 V. These peaks coincide with the calculated LUMO (lowest unoccupied molecular orbital) and LUMO+1 positions for C_{60} on Ag(111)[31] and closely resemble the experimentally measured peak positions for C_{60} on Ag(100).[32] This finding supports the above proposed model, in which the peripheral C_{60} is in contact with the Ag(111) surface. Such an arrangement is enabled because of the conformational degrees of freedom of the DTPO groups of the Pc derivative, which enclose the C_{60}. In the case of the central C_{60}, however, the d*I*/d*V* spectrum (blue curve in Figure 3a) does not match the features characteristic for C_{60} on Ag(111). It is important to note that the d*I*/d*V* spectrum taken on top of a central C_{60} residing on the Pc (inset in Figure 3) is clearly different from the superposition of d*I*/d*V* spectra taken on the peripheral C_{60} and on the Pc. Altogether, this provides strong indications that the central C_{60} is in contact with the Pc core and not with the substrate. A closer look at the spectrum reveals some distinct features:

(i) insignificant shift of the LUMO peak for the peripheral and central C_{60}
(ii) significant upward shift in energy for LUMO+1 (out of the measured range)
(iii) pronounced splitting of the LUMO state.

These observations are in contrast to the spectroscopic features observed for C_{60} coadsorbed with TPA (tetraphenyladamantane).[33] There, the coadsorption leads to a decoupling of C_{60} from the metal substrate, and thus, the splitting of the orbitals is strongly reduced, and both LUMO and LUMO+1 are shifted upward while their energy gap is preserved. Hence, we can deduce for our system that the central C_{60} is not merely decoupled from the substrate by the Pc, but also, a strong electronic interaction between the Pc and the C_{60} occurs, in analogy to the calculated electronic properties of a similar system.[9] This interaction results in the change of the energy gap between LUMO and LUMO+1. Moreover, due to this interaction, the C_{60} cage is expected to be slightly distorted. This leads to a decrease of the LUMO degeneracy, which can be observed as a splitting in the d*I*/d*V* spectra.[33]

To conclude, we have shown that C_{60}, upon deposition onto an ordered layer of ZnPc-DTPO, spontaneously binds either to the Pc core or in between two Pc molecules belonging to adjacent molecular rows. The peripheral C_{60} features properties analogous to those of C_{60} adsorbed on Ag(111), whereas the electronic properties of the central C_{60} are strongly influenced by the underlying ZnPc-DTPO. Hence, the presented Pc−C_{60} system formed by self-assembly in vacuo is an excellent example for a surface-supported donor−acceptor complex which offers itself to investigations by STM and STS at the single-molecule level. Notably, it is the specific properties of the DTPO substituents, in particular, their conformational flexibility,[26] which facilitate the direct interaction of C_{60} with the π-conjugated Pc core. The successful fabrication of a physically (i.e., noncovalently) coupled molecular architecture formed by self-assembly at surfaces and containing donor and acceptor moieties is of immense potential in the context of optoelectronic functional layers as well as molecular nanoscale devices.

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Supporting Information Available: Additional figures and experimental information. This material is available free of charge via the Internet at http://pubs.acs.org.

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